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# A review on gasification of biomass

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#### Abstract

Studies on the effect of size, structure, environment, temperature, heating rate, composition of biomass and ash are reviewed. Based on the observations reported so far, auto-gasification of biomass by the bio-oxygen and the catalytic ash would be feasible. The auto-gasification may be explained in terms of heterogeneous catalytic reaction. Better understanding of auto-gasification is possible by further studies carrying out on the effect of heating rate on auto-gasification.

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#### 1. Introduction

Amongst the renewable energies, one of the most important energy sources in near future is biomass. The third among the primary energy sources after coal and oil is the biomass [1]. Because of its wide spread availability, renewable in nature and potential in nutral in relation to global warming [2]. The potential of biomass to help to meet the world energy demand has been widely recognized. The reduction on the imported forms of energy and conservation of limited supply of fossil fuels depends upon the utilization of all other indigenous fuel energy sources. This has resulted in the use of biomass as an alternate energy source for developing countries since the economies of these countries are based largely on agricultural and forestry. Bio-chemical and thermo-chemical process are used for the recovery of energy from biomass [3]. Bio-chemical process involves bio methanization of biomass. Thermo-chemical processes are combustion, pyrolysis and gasification. Combustion burns the biomass to ash with excess air. Biomethanisation requires powdery and porous biomass with always greater than 60% moisture. In addition to biogas, the fermented biomass is very good manure for agricultural fields. The hydraulic retention time is always very high resulting in huge volume of digester. Combustion of biomass involves in burning the biomass in air at a flow rate of 4-5 kg of air per kg of biomass. This process on small-scale is always used for thermal applications. For power generation a large-scale combustion plant with steam cycle is essential for power generation. Gasification is economical at all capacities from 5kWe onwards. Therefore, there is a constant and consistent interest in the production of energy from biomass through gasification. From time to time, several observations are reported to explain the complex nature of gasification. A time has come now to revisit the gasification process to bring out the role of characterization of biomass. The present review aims at analyzing the effect of physical and chemical properties of biomass on gasification.

# 2. Gasification

It is customary to report the content of moisture, volatile matter, fixed carbon and ash as proximate analysis. Table 1 gives the proximate analysis of 13 biomasses reported by Raveendran et al. [4]. Upon heating the biomass gets dried up to 120 °C, devolatalized the volatile matter up to 350 °C and gasified the char above 350 °C. Therefore, it is customary to classify the entire gasifier process as drying, devolatiliation and gasification. Depending upon the nature of environment inert or reactive prevailing during gasification the process is called pyrolysis for inert environment and gasification for reactive environment. Pyrolysis is the devolatilization of volatile matter in inert medium to produce pyrolytic liquids, solid char and gaseous fuel. The liquid product may also be upgraded to

refined fuels. The solid char may be used as a fuel. The gaseous fuel is high in hydrocarbons with high calorific value. Since the bulk density and calorific values of pyrolytic liquid and solid char are very high they have high-energy density compared to original mass [5]. When the environment is reactive (air) complete gasification of biomass takes place yielding gaseous fuel and ash.

#### 3. Variables

The variable affecting the rate of gasification are to be identified and quantified. The variables are given below:

Sl. no.	Variable	Characteristics					
1	Size	Small	Big				
2	Shape	Powdery	Lump				
3	Structure	Porous	Non-porous				
4	Environment	Inert	Reactive				
5	Flow of medium	Static	Continuous				
6	Heating rate	Slow	Fast				
7	Temperature	$<$ 500 $^{\circ}$ C	> 500 °C				
8	Ash	Catalytic	Non-catalytic				

Since pyrolysis and gasification of biomass are thermochemical processes, the temperature and rates of heating have pronounced effects on the weight loss of biomass. Thermogravimetric analysis (TGA) measures and records the weight loss of sample biomass as the temperature is raised at desired uniform rate. In addition the effect of environment such as inert and reacting atmosphere

Table 1 Proximate analysis of biomasses [4]

Sl. no.	Biomass	VM (daf) (%)	Ash (db) (%)	Fixed carbon (100–VM) (%)
1	Bagasse	84.2	2.9	15.8
2	Coconut coir	82.8	0.9	17.2
3	Coconut shell	80.2	0.7	19.8
4	Coir pith	73.3	7.1	26.7
5	Corn cob	85.4	2.8	14.6
6	Corn stalks	80.1	6.8	19.9
7	Cotton gin waste	88.0	5.4	12.0
8	Groundnut shell	83.0	5.9	17.0
9	Millet husk	80.7	18.1	19.3
10	Rice husk	81.6	23.5	18.4
11	Rice straw	80.2	19.8	19.8
12	Subabul wood	85.6	0.9	14.4
13	Wheat straw	83.9	11.2	16.1

with and without flowing can be studied. For determining the characteristics of pyrolysis and also kinetic parameters, TGA is used extensively. Kinetic parameters are calculated using the net weight loss with simplifying assumptions which do not necessarily correspond to the complex chemical reaction in the thermal degradation of biomass. However, TGA data provide useful comparisons of reaction parameters such as temperature and heating rates.

#### 3.1. Size

Smaller the biomass size better would be the heat transfer. The temperature would be uniform resulting in reaction taking place throughout the particle. Whenever reaction controls the gasification, the rate of reaction will be maximum and increases exponentially with temperature. However, there is a limitation on the size above which heat transfer would be controlling. Maa and Bailie [6] have shown that the pyrolysis of cellulose material is reaction-controlled for size less than 0.2 cm, for sizes 0.2–6 cm both heat transfer and reaction control, whilst above 6 cm heat transfer controls.

# *3.2. Shape*

Bio-residues are generally powder in nature. At present they are pelletized before gasification so as to reduce the volume of gasifier. Pelletization consumes power thus reducing the available energy. Lumps on the other hand can be gasified conveniently. However, lumps beyond 6 cm size are not suitable. In order to have uniform rate of gasification yielding uniform composition of producer gas, the lumps are cut into small chips having size less than 2.5 cm. Chipping is also an energy consuming operation.

# 3.3. Structure

If the biomass is highly porous, the surface area for reaction is very high and the diffusion of the reactant/product would be easy. Uniform temperature could be achieved throughout biomass resulting in continuous reaction at all portions of biomass yielding uniform composition of product gases. When the biomass is less porous, the temperature varies from the maximum at the exterior to the minimum at the interior. The reaction takes place only at the exterior surface. This surface shrinks with reaction. Because of the non-uniformity in temperature, drying, pyrolysis and gasification take place simultaneously yielding non-uniform composition of gases.

Grønli et al. [7] have studied thermogravimetric analysis and devolatilization kinetics of hard woods such as alder, beech, birch and oak, and soft woods such as Douglas fir, pine A, pine B, redwood and spruce. They have observed that in the case of soft woods, the decomposition starts at lower temperature, the maximum temperature of weight

loss for hemicellulose is higher and hemicellulose & cellulose zones are wider.

#### 3.4. Environment

Generally, it is observed that reactive environment (air/oxygen) results in complete gasification of biomass while inert environment (nitrogen/argon) aids devolatilization (pyrolysis) yielding more char. Pyrolysis of biomass has attracted the attention of many investigators [8,9] as it yields solid, liquid and gaseous fuel from biomass.

Commercial gasifiers employ air at substoichiometric quantity to generate producer gas. Depending upon the type of contact between biomass and air, the gasifier is called down draft, updraft or cross flow gasifier. Each type has its own advantages and disadvantages in generating quality producer gas. Thus, the understanding on the effect of environment on gasification has come to the natural end. Hence, the present gasifiers produce gases with low calorific values due to dilution by nitrogen.

# 3.5. Flow of medium

Williams and Besler [8,9] have observed that the secondary degradation of char to gases can be prevented in pyrolysis of biomass by sweeping away the devolatilized gases by inert gases such as nitrogen. This yields more char equal to fixed carbon content in the biomass. Therefore, many investigators have carried out the pyrolysis studies with flowing nitrogen.

Safi et al. [10] have carried out studies on global degradation kinetics of pine needles in air. An air flow rate of 50 ml/min was maintained. The char obtained at different heating rates were less than the available fixed carbon, due to the presence of reactive medium such as air.

If the medium were static, then there is a possibility of secondary degradation of char taking place. This may result in complete gasification of biomass. However, no attempt is reported so far on the effect of static inert or static reactive medium on the gasification of biomass.

#### 3.6. Heating rates

Bridgwater [5] reported the influence of pyrolysis reaction parameters such as temperature and heating rates to determine the yield and composition of the derived products. In fast pyrolysis with high heating rates of up to  $1000\,^{\circ}\text{C/min}$  at temperature below  $650\,^{\circ}\text{C}$  and with rapid quenching the liquid, intermediate products of pyrolysis condenses without further breaking down higher molecular weight species into gaseous products. Formation of char is minimized by high heating rates. Gaseous products form at high heating rates to high maximum temperature. If the desired end product is the liquid hydrocarbon or bio-oil, fast pyrolysis is preferred. Fluidized bed, cyclonic, entrained flow, vortex and ablative reactors are recommended for fast pyrolysis.

Slow pyrolysis requires low heating rates and low maximum temperature. Maximum yield of char via secondary coking and repolymerization reaction is observed at slow heating rates coupled with a low final maximum temperature (less than 500 °C) and with long gas and solid residence times. Therefore, slow pyrolysis has been used for the production of char. Fixed bed reactor, multiple hearths and rotary kiln are used for slow pyrolysis.

Even though the rate of purging of gaseous products to prevent the secondary reaction influences the pyrolysis, no attempt has been made so far to evaluate its effect. William and Besler [9] have carried out a detailed study on the influence of temperature and heating rate on slow pyrolysis of biomass in a static batch reactor at heating rates of 5, 20, 40 and 80 K/min to a final temperature of 300, 420, 600 and 720 °C with nitrogen as purging gas. Slow pyrolysis has yielded aqueous, oil, gas and char. The gaseous, liquid and solid products of pyrolysis are analyzed for composition, yield and calorific value.

The observations made are as follows:

- A decrease in the yield of char and a corresponding increase in the yield of oil and gas resulted with increase in temperature for each heating rate.
- At 420 °C and above, the aqueous yield remained virtually constant at about 37 wt%.
- Very high char yield has been obtained at 300 °C as char has retained partially pyrolysed material such as hydrocarbons of high molecular weight.
- The high molecular weight hydrocarbon within char volatilizes and degrades thermally as the temperature was increased.
- The oil yield increases steadily from 300 to 720 °C at all heating rates.
- The oils are highly oxygenated.
- An increase in carbon and hydrogen and a decrease in sulfur and oxygen contents of the oil with heating rates were observed.
- The gas yield also increases with temperature at all heating rates.
- The char yield decreases with temperature and with heating rates.
- The calorific values of oils and char were essentially independent of heating rates and were found to be an average 23 and 32 MJ/kg, respectively.
- The yields of CO, CO<sub>2</sub>, H<sub>2</sub> CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> increased with heating rates.
- Total calorific values were 13.6, 15.7, and 15.8 MJ/m<sup>3</sup> at heating rates of 5, 20, 40 and 80 K/min, respectively.
- The calorific values of gases were fairly independent of heating rates above 5 K/min.
- Water and oil were evolved throughout the higher temperature.

Safi et al. [10] have studied the global degradation kinetics of pine needles in air. TGA was carried out with

10 mg of sample wood in air flowing at 50 ml/min at 5, 10, 15, 25 and 30 K/min. It is interesting to note that three temperatures for maximum weight loss were observed unlike wood and rice husk pyrolysis reported by William and Besler [9]. Further there is a lateral shift in the temperatures for maximum weight loss for heating rates 5 and 10 K/min. The temperature for maximum weight loss decreases with increase in heating rates from 15 to 30 K/min. It is evident from the above that the heating rates influence the rate of gasification considerably.

# 3.7. Temperature

Two temperature ranges are normally selected above and below 500 °C. Generally temperatures above 500 °C are chosen for reduction of carbon dioxide by carbon to carbon monoxide. Therefore, pyrolysis of biomass is carried out at temperature less than 500 °C for the maximum yield of char with inert medium flowing. Complete gasification is achieved at temperature above 500 °C with air flowing.

# 3.8. Ash

Ash contains mineral matters. The composition of ash in bio-residues as reported by Raveendran et al. [4] has been reproduced in Table 2.

Shafizadeh [11] has observed that the presence of even very low concentrations of impurity have been shown to either catalyze or inhibit the degradation. Further the presence of trace metals results in shifts to lower temperature for the thermal decomposition of cellulose.

Byun et al. [12] have reported that the oxides of copper/zinc/aluminum catalyze the water gas reaction at lower temperature (200–300 °C). Raveendran et al. [4] have studied the influence of mineral matter on pyrolysis by demineralizing the biomass and then impregnating with salts and has reported the following:

- 1. In cases of demineralized coir pith, groundnut shell and rice husk, the char yield increases.
- 2. In cases of demineralized corn cob and wood, the char yield decreases.
- 3. Demineralized rice husk yielded higher char than coir pith and groundnut shell.
- 4. Liquid yield increases for all demineralized biomass.
- 5. Coir pith, groundnut shell and rice husk yield less char when the demineralized biomass is impregnated with zinc chloride and potassium chloride salts.
- 6. In all cases, the liquid yield decreases and the gas yield increases due to salt impregnation.
- 7. Zinc chloride impregnation has increased the gas yield and has reduced liquid yield.
- 8. Higher the salt concentration, the lower is the liquid yield.
- 9. Only cation effects the changes in liquid and gaseous yield.

Table 2
Ash composition of biomass: major (ppmw dry biomass) [4]

Sl. no.	Biomass	Al	Ca	Fe	Mg	Na	K	P	Si	CO	Cr	Cu	Mn	Ni	S	Zn
1	Bagasse	_	1518	125	6261	93	2682	284	17340	_	_	18	9	16	60	16
2	Coconut coir	148	477	187	532	1758	2438	47	2990	0.6	2.0	68	4	2	64	25
3	Coconut shell	73	1501	115	389	1243	1965	94	256	0.5	0.3	5	1	13	35	9
4	Coir pith	1653	3126	837	8095	10564	26283	1170	13050	3.2	0.2	1239	27	22	476	40
5	Corn cob	-	182	24	1693	141	9366	445	9857	_	_	Trace	19	6	15	11
6	Corn stalks	1911	4686	518	5924	6463	32	2127	13400	8.0	11	32	12	13	564	32
7	Cotton gin waste	_	3737	746	4924	1298	7094	736	13000	_	_	Trace	38	10	58	22
8	Groundnut shell	3642	12970	1092	3547	467	17690	278	10960	2.3	6	11	44	11	299	52
9	Millet husk	-	6255	1020	11140	1427	3860	1267	150840	_	_	Trace	38	49	317	94
10	Rice husk	_	1793	533	1612	132	9061	337	220690	_	_	21	108	32	163	1244
11	Rice straw	-	4772	205	6283	5106	5402	752	174510	_	_	Trace	463	45	221	47
12	Subabul wood	-	6025	614	1170	92	614	100	195	_	_	1	2	1	66	40
13	Wheat straw	2455	7666	132	4329	7861	28930	214	44440	-	-	7	25	25	787	18

Table 3 Components of biomass [4]

Sl. no.	Biomass	Ash	Holocellulose	Cellulose	Hemicellulose	Lignin	Extractives	Total (holo)	Total (hemi)
1	Bagasse	2.9	65.0	41.3	22.6	18.3	13.7	99.9	98.8
2	Coconut coir	0.8	67.0	47.7	25.9	17.8	6.8	111.7	99.0
3	Coconut shell	0.7	67.0	36.3	25.1	28.7	8.3	98.7	100.1
4	Coir pith	7.1	40.6	28.6	15.3	31.2	15.8	94.8	98.1
5	Corn cob	2.8	68.2	40.3	28.7	16.6	15.4	102.9	101.8
6	Corn stalks	6.8	63.5	42.7	23.6	17.5	9.8	97.6	100.5
7	Cotton gin waste	5.4	90.2	77.8	16.0	0.0	1.1	86.7	100.2
8	Groundnut shell	5.9	55.6	35.7	18.7	30.2	10.3	102.0	100.7
9	Millet husk	18.1	50.6	33.3	26.9	14.0	10.8	96.5	104.1
10	Rice husk	23.5	49.4	31.3	24.3	14.3	8.4	96.5	101.8
11	Rice straw	19.8	52.3	37.0	22.7	13.6	13.1	98.8	106.2
12	Subabul wood	0.9	65.9	39.8	24.0	24.7	9.7	101.2	99.0
13	Wheat straw	11.2	55.8	30.5	28.9	16.4	13.4	96.7	100.4

It is evident that from observations 1–4, the absence of mineral matters due to deashing has yielded more char and liquid fuels. Observations 5–9, on the other hand, establish a decrease in the yield of char and liquid fuels due to impregnation of deashed bio-residues by salts like zinc chloride.

From the composition of ash for various bio-residues given in Table 2, it is seen that ash contains mainly oxides of metals. These metal oxides impregnated on porous silica in the ash, catalyze the gasification.

# 4. Components of biomass

Cellulose, hemicellulose and lignin and extractives are found to be the major components of biomass. Raveendran et al. [4] have reported the composition of biomass in terms of these components. Table 3 reproduces these results for 13 biomasses. The thermal degradation of biomass and samples of cellulose, hemicellulose and lignin has been studied extensively using TG analyzer. Most of the investigators have studied the effects of heating rates and temperature on pyrolysis using TG analyzer.

Since the main objective of their studies is to get maximum char and combustible volatiles, TGA studies were reported to have been carried out in inert atmosphere with flowing nitrogen to purge out the product gases thus preventing the secondary reactions. Low heating rates with low final temperature were employed to achieve slow pyrolysis of biomass and samples of cellulose, hemicellulose and lignin.

Williams and Besler [8,9] have carried out TGA of wood and rice husks and samples of cellulose, hemicellulose and lignin at heating rates of 5, 20, 40 and 80 K/min with nitrogen flowing to purge out the product of gases.

The following observations were made at all heating rates:

- Hemicellulose represented by xylan decomposes between 220 and 320 °C and continued heating up to 720 °C resulted in yielding char approximately 20 wt% of the original hemicellulose.
- Cellulose decomposes between 250 and 360 °C and has yielded char approximately 8 wt% of the original cellulose after heating to 720 °C.

• Lignin undergoes gradual decomposition between 80 and 500 °C yielding char 55 wt% of the original lignin after heating to 720 °C.

From the TGA data, DTG curves have been drawn at different heating rates for wood, cellulose, hemi cellulose and lignin. The following was observed:

- Only one temperature for maximum weight loss has been observed for hemicellulose, cellulose and lignin.
- Two temperatures for maximum weight losses were observed for wood (one closer to hemicellulose maximum temperature and the other to cellulose).
- As heating rate increases there is a lateral shift in the temperatures for maximum weight loss due to combined effects of heat transfer at the different heating rates and the kinetics of the decomposition resulting in delayed decomposition.

# 5. Composition of biomass

Every biomass has carbon, hydrogen and oxygen in major quantities. These are represented as ultimate analysis. Raveendran et al. [4] have reported the composition of 13 biomasses. These are reproduced in Table 4. The chemical formula for the biomass is generally represented by  $C_xH_yO_z$ . The coefficients of x, y and z are calculated for each of the biomass and are also given in Table 4 along with average values. Comparing the average value with those of individual biomass, it is evident that these coefficients are more or less same in all the cases. This observation is further supported by the closeness of calorific values of these biomasses given in Table 4.

A closer look at the carbon and oxygen contents of these biomasses reveals that every biomass has oxygen to convert carbon to oxides of carbon either partially or completely. Using the data the percentage of carbon that could have been converted to CO by oxygen available in the biomass (bio-oxygen) was calculated for each of biomass and is given in the last column of Table 4. It is evident that 56.5-87% of carbon could have been converted to CO depending upon the bio-oxygen available. And, 13–43.5% of carbon is vet to be converted. However, it is noteworthy that carbon is also consumed in the formation of methane and hydrocarbon and in the water gas reaction. Therefore, it is possible to gasify the biomass in the absence of air theoretically. This paves way for auto-gasification namely conversion of solid combustible matter in the biomass by the bio-oxygen itself.

# 6. Summary

From the foregoing review, the following observations could be arrived at:

- Biomass is a compound consisting of C,H,O in major quantity.
- 2. These constituents are held as chemisorbed matter on the fibrous ash matrix.
- 3. The composition of C, H and O is more or less same in all biomasses.
- 4. The calorific values are also nearly same.
- 5. Yet the quality and quantity of gasification varies with biomass.
- 6. Environment results in pyrolysis or complete gasification of biomass.
- 7. Flow of medium increases the yield of char preventing secondary degradation reactions.

Table 4 Ultimate analysis of biomass [4]

Sl. no.	Biomass	Ultimate analysis (wt%)					Density	X	y	Z	Percentage
		С	Н	N	О	(MJ/kg)	$(kg/m^3)$				conversion of carbon
1	Bagasse	43.8	5.8	0.4	47.1	16.29	111	3.65	5.8	2.94	81
2	Coconut coir	47.6	5.7	0.2	45.6	14.67	151	3.97	5.7	2.85	72
3	Coconut shell	50.2	5.7	0.0	43.4	20.50	661	4.18	5.7	2.71	65
4	Coir pith	44.0	4.7	0.7	43.4	18.07	94	3.67	4.7	2.71	74
5	Corn cob	47.6	5.0	0.0	44.6	15.65	188	3.97	5.0	2.79	70
6	Corn stalks	41.9	5.3	0.0	46.0	16.54	129	3.49	5.3	2.88	82.3
7	Cotton gin waste	42.7	6.0	0.1	49.5	17.48	109	3.56	6.0	3.10	87
8	Ground nut shell	48.3	5.7	0.8	39.4	18.65	299	4.03	5.7	2.46	61.2
9	Millet husk	42.7	6.0	0.1	33.0	17.48	201	3.56	6.0	2.063	58
10	Rice husk	38.9	5.1	0.6	32.0	15.29	617	3.24	5.1	2.0	62
11	Rice straw	36.9	5.0	0.4	37.9	16.78	259	3.08	5.0	2.37	82.4
12	Subabul wood	48.2	5.9	0.0	45.1	19.78	259	4.02	5.9	2.82	70.2
13	Wheat straw	47.5	5.4	0.1	35.8	17.99	222	3.96	5.4	2.24	56.5
Avera	ge	44.6	5.5	0.3	41.8	17.32	253.84	3.72	5.49	2.61	70.89

<sup>&</sup>lt;sup>a</sup>Higher heating value.

- 8. In porous biomass, the reaction could be taking place continuously due to uniform temperature.
- 9. In non-porous biomass or in lumps, drying, devolatilization and gasification takes place simultaneously due to non-uniform temperature.
- 10. In practice size less than 2 mm, chemical reactions controls, between 2 and 60 mm, chemical reaction and heat transfer control and above 60 mm, heat transfer controls the gasification.
- 11. Heating rate influence the quality of gasification and quantity of products.
- 12. Every biomass has sufficient quantity of oxygen (biooxygen) to convert the solid combustible matter in it to gaseous fuel.
- 13. Ash catalyzes the gasification.
- 14. Porous biomasses are gasified completely into ash at temperatures less than  $600\,^{\circ}$ C.
- 15. In porous biomasses, thermo-chemical conversion of solid combustible matter into gaseous fuel by bio-oxygen and catalytic ash.
- 16. Gasification by bio-oxygen in the presence of ash is called "auto-gasification".

# 7. Plausible mechanism of gasification

A bird's view on the heterogeneous catalytic reaction would help in understanding gasification better. In heterogeneous catalytic reaction, the following steps are taking place:

- 1. Diffusion of reactants through the gas film surrounding the catalytic particle.
- 2. Diffusion of reactants through the pores of the catalyst to the reaction sites.
- 3. Chemisorption of reactants on the reaction sites.
- 4. Reaction between the chemisorbed reactants on the reaction sites.
- 5. Desorption of products from the reaction sites making the sites available for fresh reactants to get chemisorbed.
- 6. Diffusion of products through the pores to the surface of the catalyst.
- 7. Diffusion of products through the gas film surrounding the catalyst particle.

Steps 1, 2, 6 and 7 are considered to be physical steps as no new compound is formed in these steps. Steps 3–5 are chemical steps producing new compounds. Since, all these steps are taking place in series, the slowest step is considered to be controlling the reaction.

The activity of the catalyst depends upon the number of sites and activity level in each site. The activity level of site decides the product distribution while number of sites determines the rate of reaction. Temperature has exponential effect on these factors.

From the observations made, the gasification may be viewed as a heterogeneous reaction catalysed by ash. The reactants may be chemisorbed on the ash catalyst. Because

of these steps 1–3 of heterogeneous catalysts will not be existing in the gasification. All other steps will be taking part in the reaction. The following phenomena may be assumed to be taking place in gasification:

- 1. Upon heating, the sites on the ash catalyst get activated.
- 2. Depending upon the temperature, the number of sites activated and their activity level vary.
- 3. Carbon, hydrogen and oxygen molecules chemisorbed on the ash matrix get reacted.
- 4. Depending upon the activity level of the site carbon, hydrogen and oxygen give rise to various composition of CO, CO<sub>2</sub>, hydrocarbons, water, methane, etc.
- 5. Char produced may react with water vapor to produce CO and H<sub>2</sub> in the presence of catalytic ash.
- 6. The products thus formed diffuse through pores in the catalytic ash.
- 7. The products further diffuse through the gas film surrounding the biomass.
- 8. If the product gases are swept away by purging gases such as N<sub>2</sub> or argon, as and when they formed, then the secondary degradation such as conversion of carbon to CO and H<sub>2</sub> would not have taken place. Several investigators have reported this [8,9].

# 8. Conclusion

It is obvious from the above discussion that autogasification of biomass into gaseous fuel by bio-oxygen and catalyst ash is feasible. The attainment of uniform temperature and the absence of flowing medium help secondary degradation are essential in achieving this. Therefore, further studies on the effect of heating rate on auto-gasification would be the key to the quality and quantity of the products of gasification.

#### References

- [1] Werther J, Saenger M, Hartage EU, Ogada T, Siagi Z. Combustion of agricultural residues. Prog Energy Combust Sci 2000;26:1.
- [2] Abbas T, Costem PG, Lockwood FC. Solid fuel utilization: from coal to biomass. In: 26th symposium (international) on combustion, The Combustion Institute, Pittsburgh, PA; 1996. p 3041–58.
- [3] Grassi G, Gosse G, Dos-Santos G. Biomass for energy and industry. London: Elsevier Applied Science; 1990.
- [4] Raveendran K, Ganesh A, Khilar KC. Influence of mineral matter on biomass pyrolysis characteristics. Fuel 1995;74(12):1812–22.
- [5] Bridgwater AV. Biomass pyrolysis technologies, biomass for energy and industry. London: Elsevier Applied Science; 1990.
- [6] Maa PS, Bailie RC. Influence of particle sizes and environmental conditions on high temperature pyrolysis of cellulose material. Combust Sci Technol 1973;7:257–69.
- [7] Grønli MG, Varhegyi G, Di Blasi C. Thermogravimetric analysis and devolatilization kinetics of wood. Ind Eng Chem Res 2002;41: 4201–8.
- [8] Williams PT, Besler S. The pyrolysis of rice husks in a thermo gravimetric analyzer and static batch reactor. Fuel 1993;72: 151–9.

- [9] Williams PT, Besler S. Influence of temperature and heating rate on the slow pyrolysis of biomass. Renew Energy 1996;7: 233–50.
- [10] Safi MJ, Mishra IM, Prasad B. Global degradation kinetics of pine needles in air. Thermochem Acta 2004;412:155–62.
- [11] Shafizadeh F. Pyrolysis and combustion of cellulosic material. Adv Carbohydr Chem 1968;23:419–74.
- [12] Byun I-S, Choi O-L, Choi J-G, Lee S-H. In situ photoacoustic study of water gas shift reaction over magnetite/chromium oxide and copper/ zinc oxide catalysts. Bull Korean Chem Soc 2002;23(11):1513-7.